

MS17-1-4 Elucidating the local structure of poorly crystalline and amorphous carbon nitride materials using energy-filtered electron radial distribution function analysis and low electron dose HRTEM

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Abstract

Understanding the structure of carbon nitrides is a long-standing challenge, since many of them are complex, often poorly crystalline or even amorphous materials, which are usually difficult to characterize by standard diffraction methods. Still, detailed knowledge about their structure (especially local ordering) is key to control properties of existing carbon nitrides and design new compounds. In this respect, electron radial distribution function (eRDF) analysis is becoming more and more attractive as a fast, easy accessible tool to quantitatively describe and compare the local structure of materials. The eRDF is usually obtained from electron total scattering data, which can be collected on any standard transmission electron microscope within a few seconds making this technique easily accessible to a lot of users. The zero-loss-energy filtering method that we applied allows mainly elastically scattered electrons to contribute to the diffraction signal, improving the signal-to-noise ratio about 5 times and thus allowing to obtain reliable energy-filtered eRDFs even from amorphous materials. Here, I present the application of energy-filtered electron radial distribution function (EF-eRDF) analysis, combined with low-dose transmission electron microscopy imaging and X-ray powder diffraction, to study several members of the carbon nitride family (from poorly crystalline poly(heptazine imide) salts (M-PHI, M=K, Na, Mg) to amorphous nitrogen doped carbons (a-CN)).

Starting structural models of M-PHI (M=K, Na, Mg) salts were created based on HRTEM data and a general assumption about the structure. A stacking of polyheptazine imide layers on top of each other with M atoms placed within and in between the layers allows the formation of channels along the c-direction. However, problems with determining the exact metal positions, as well as particular anisotropic broadening of the peaks, clearly pointed to the presence of defects in the systems. A detailed analysis of the eRDFs showed that the average coherence length (ACL) of M-PHI (M=K, Na, Mg) salts is about 5 nm. Peak positions in the eRDFs coincide with the models obtained from XRD Rietveld refinement only up to 4.2 Å. As found by Reverse Monte Carlo refinement of the eRDFs and HRTEM image analysis, the layers are not stacked perfectly but display 2-8 degrees of rotational disorder and also partial disorder of the polyheptazine backbone within the layer. The presence of this disorder without breaking the main channel structure of M-PHI, promotes their high catalytic activity. One can see the striking difference in the ACL of M-PHIs compared to a-CN, for which it is around 7 Å, indicating that only short-range order up to the 3rd coordination sphere is present in the amorphous CN covalent framework. The main C-N and C-C peak positions are common for both M-PHI and a-CN up to 4.5 Å, but in the case of a-CN, the peaks are broader. The limited size of the ordered regions in a-CN facilitates their high sorption capabilities.

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